SCIENCE FOR GLASS PRODUCTION

SLIP TECHNOLOGY FOR FABRICATION OF HIGHLY POROUS CELLULAR GLASS MATERIAL

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The possibility of using slip technology in production of highly porous cellular materials from alumino-borosilicate glass was demonstrated. The factors that affect the rheology and stability of the slip system and the structural and strength characteristics of the finished material were identified. The materials obtained can be used as substrates in chromatography, for treatment of liquids and gases in filtration, etc.

High-strength cellular ceramic and metallic materials (HSCM) are widely used in modern engineering as filters for treating gases and liquids, catalyst supports, substrates in chromatography, acoustic vibration dampers, firewalls, and in mass exchangers.

One widespread method of fabricating HSCM is duplicating the structure of a lattice-honeycomb polymer — polyurethane foam (PUF) — using slip technology and subsequent breakdown of PUF during heat treatment (see Diagram 1). Despite the difficulty in obtaining large stock (greater than 300 mm in length and width) without warping and shrinkage cracks, this method has been widely used in HSCM technology [1]. Due to duplication, the material acquires the cellular structure of foamed PUF. The only difference is the microporosity and channel porosity in the finished sample [2].

The interest in HSCM as a promising material for use in different branches of the chemical and construction industries is due to a number of factors:

the possibility of regulating the cell size in a wide range (0.5 – 5.0 mm);

the combination of macro-, microporosity (0.05 – 0.25%), and channel porosity;

sufficiently high mechanical strength (up to 1.5 MPa for ceramic and up to 5 MPa for metallic materials);

possibility of realizing high flow rates of liquids and gases through the material at low power consumption for pumping.

In addition, HSCM are not the same with respect to the porosity (up to 98%) and permeability (up to 10^{-9} m^2) [1, 3].

Due to the high demand for HSCM, it has become necessary to create materials with structural and strength characteristics as good as the ceramic and metallic analogs. For this reason, developing glass HSCM is a pressing problem. The new materials will hypothetically be widely used in the
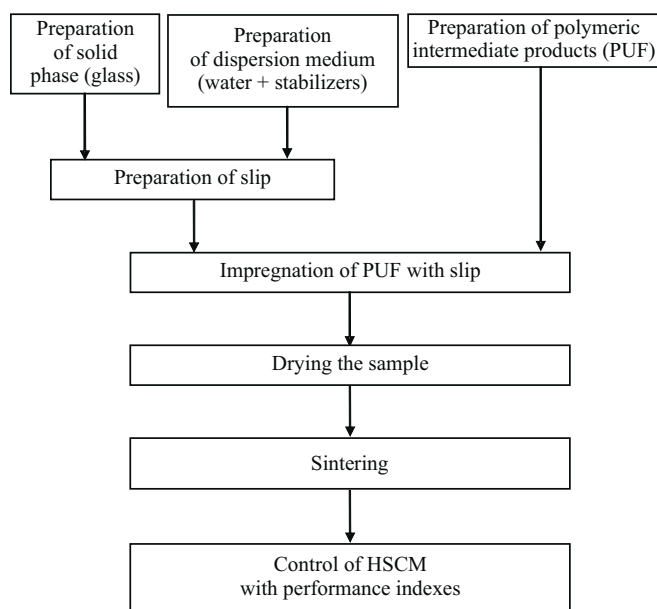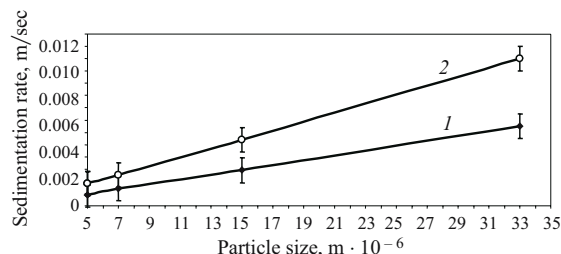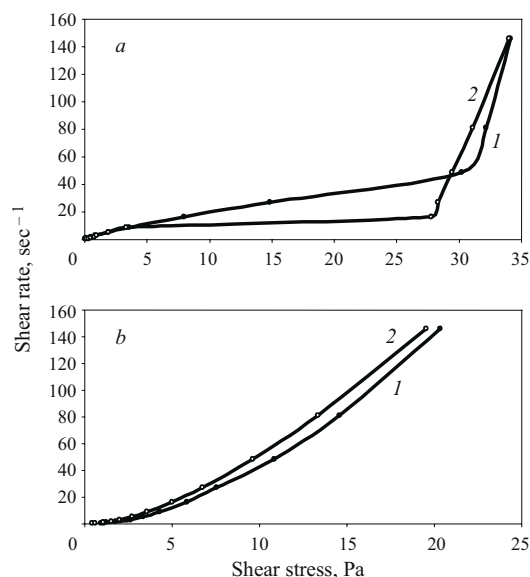

Diagram 1. Process scheme for production of HSCM.

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Fig. 1. Sedimentation stability of slip systems in PVA (*1*) and CMC (*2*).

Fig. 2. Thixotropy of slip system in PVA (*a*) and CMC (*b*): *1* and *2*) flow curves in loading and unloading, respectively.

chemical industry as substrates in chromatography and filters for treating liquids and gases [4].

Aluminoborosilicate glass HSCM are being developed at D. I. Mendeleev Russian Chemical Engineering University.

The glass was melted at $1400 – 1500°C$. The granulate obtained was wet-ground into a polydisperse powder with a particle size of less than 20 μm in a ball mill. The slip consisted of a disperse phase (glass powder) and a dispersion medium — polyvinyl alcohol (PVA) or carboxymethyl-cellulose (CMC). The dried stock underwent step heat treatment up to $700 – 720°C$ for $4 – 5$ h.

In developing this material, selecting the optimum composition of the aluminoborosilicate glass was the initial problem. Of the six proposed compositions with a molar content of B_2O_3 from 4 to 8% and gradual substitution of SiO_2 by Al_2O_3, the composition with the following properties was used for the studies as a result of the experiments:

TCLE of $(80 – 85) \times 10^{-7} K^{-1}$, which corresponds to high thermal stability (up to $200°C$);

the glass transition and initial deformation temperature corresponding to the temperature range of degradation of

PFU (glass transition temperature of $600 – 620°C$, initial deformation temperature of $740 – 760°C$);

weight losses in boiling in water for 1 h of $0.20 – 0.22\%$ (hydrolytic class III).

The next, most complicated stage, was developing the optimum slip system.

Qualitative impregnation of PFU can only be attained with good fluidity, thixotropy, high sedimentation and aggregate stability of the slip, and an important solid phase content [5].

The solid phase had the greatest effect on the rheology of the disperse systems. As practice showed, for attaining a fluid thixotropic pseudoplastic stable slip system, the particles of the disperse phase must be round in shape and $5 – 10$ μm in size (specific surface area of $7 – 10$ m^2/g) [6]. The requirement for the particle shape is due to the fact that real particles can be porous, in the form of chips, crystal aggregates, rods, and fibres and can have small hollows, protuberances, and sharp edges. The values of the viscosity and sedimentation rate of nonspherical particles differed from the experimental data obtained for spherical particles due to the larger specific surface area of the particles in comparison to round particles, the change in the reaction forces between them, the amount of bound liquid phase, and the effective volume of the solid phase.

Thixotropy (decrease in the viscosity with an increase in the load) can arise in systems whose particle size does not exceed 5 μm. This is due to the fact that Brownian motion does not arise in the transition from gel to sol in larger particles [5]. A decrease in the particle size also favorably affects the stability of the slips, but significantly worsens their fluidity and increases the viscosity [2].

The stability determines the resistance of the slips to peeling for a certain time. The sedimentation stability is related to precipitation of particles under the effect of gravity and their concentration in the slip. A particle acquires aggregate stability when the repulsive forces predominate over forces of molecular attraction when charged particles move together [5]. Slip systems in PVA have better sedimentation stability than slips in CMC, which is demonstrated by the sedimentation rate of particles of the solid phase (Fig. 1).

The studies of slip systems in PVA (5%) and CMC (6%) showed that the thixotropic properties in the systems in PVA were more pronounced than in the systems in CMC (Fig. 2). With a 5 wt.% PVA content in the slip disperse medium, the adhesive properties of PVA could be maximally manifested without significantly affecting the viscosity of the suspension [2].

It is also necessary to consider the wettability of the solid phase. With poor wetting, the air inclusions in the slip can increase. In addition to the distribution of air in the liquid, it is in contact with particles, increasing the so-called effective volume of solid phase, so that the viscosity of the slip can change. On the other hand, the air adsorbed on the surface of the particles perturbs the integrity of the surface layer. All of

this negatively affects the strength and shrinkage characteristics of HSCM. For this reason, only the slip system in PVA (5%) was used for the further studies [5].

Five systems with ratios of solid to liquid phase (S/L) of 2.0, 2.1, 2.3, 2.5, and 2.7 were investigated to select the optimum concentration of slip. The optimum concentration of slip was selected based on the quality of impregnation: S/L = 2.2 – 2.4. The optimum yield points of the system correspond to these optimum S/L ratios. The stress limit after which a disperse system breaks down and becomes unsuitable for application on a polyurethane foam substrate is determined with the limiting shear stress (Fig. 3a) [6].

In the concluding stage, we selected the optimum temperature-time conditions for sintering the material. The following factors were taken into consideration:

temperature of total breakdown of PUF: 620 – 640°C;

glass transition temperature: 620°C;

initial deformation temperature: 740 – 760°C.

Termination of the sintering regime (final temperature) was monitored based on the overall porosity, density, and mechanical and chemical strength of the HSCM.

The studies of sintered samples showed that holding for a longer time at the final temperature increased the apparent viscosity from 0.23 to 0.54 g/cm^3 and the mechanical strength from 0.7 to 0.8 MPa and decreased the losses in boiling in 95% HCl from 1.27 to 1.10%.

At the same time, the strength decreased from 85 to 79% and the shrinkage increased from 20 to 50%.

The following conclusions were drawn from these studies:

use of 5% PVA causes optimum wetting of the glass and better adhesion to polyurethane foam;

the particle size of the polydisperse powder should not exceed 10 μm;

the optimum ratio is S/L = 2.2 – 2.4;

the plastic viscosity and yield point at the optimum S/L ratio are 0.4 – 0.55 Pa · sec (Fig. 3b) and 25 – 33 Pa, respectively;

the temperature-time sintering regime at the maximum temperature of 710°C and holding at this temperature for 20 min ensures high porosity of the samples with acceptable mechanical strength.
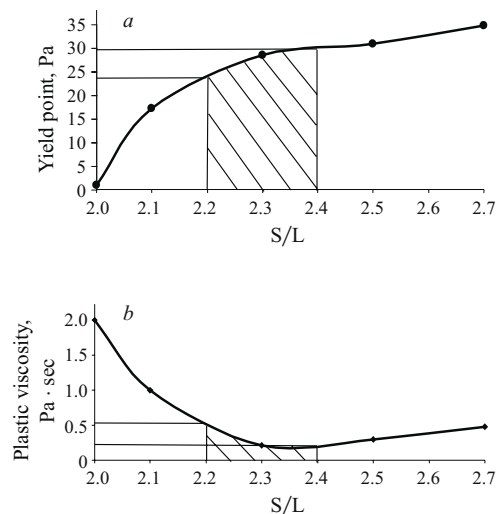
Fig. 3. Optimum yield point (*a*) and optimum plastic viscosity (*b*) of the slip system in PVA.

The cellular material obtained had the following properties: porosity of 85%, weight losses in boiling in 95% HCl of 1.27%, apparent density of 0.28 g/cm^3, shrinkage of 50%, and mechanical strength of 0.78 MPa.

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